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Polyaniline microtubes synthesized via supercritical CO_2 and aqueous interfacial polymerization

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Abstract

We report a new route to prepare polyaniline (PANI) microtubes via supercritical (SC) CO_2/aqueous interfacial polymerization. The synthesis is based on the well-known chemical oxidative polymerization of aniline in an acidic environment, with ammonium peroxydisufate (APS) as the oxidant, and sodium dodecyl sulfate (SDS) surfactant was used as the template. The main feature of this route is that the monomer (aniline) which is dissolved in SC CO_2 phase, slowly polymerized at the interface of SC CO_2 and aqueous solution to form the PANI microtubes. The morphologies, phase structure, composition and some properties of PANI microtubes were characterized by TEM, SEM, XRD, IR, XPS UV–vis and SYSTEM DM digital multimeter, respectively.

Keywords: Polyaniline; Interfacial polymerization; SC CO_2; XRD

1. Introduction

In the past 15 years, conducting polymer PANI has been extensively studied due to its unique electrical, electrochemical, and optical properties, which enable its wide use in diverse areas such as energy storage [1], electronics [2], sensors [3], and separation science [4]. Recently, much attention has been paid to low-dimensional PANI nanostructres, including nanofibers and nanotubes [5]. The PANI nanofibers and nanotubes are usually prepared by polymerization of monomers in the presence of soft [6] and hard [7] templates. Recently, Huang et al. [8,3] have reported interfacial polymerization method to synthesize sub-50 nm diameters fibers of PANI at the interface of organic/aqueous solution, respectively. Wang's group successfully prepared the chiral PANI nanofibers by oligomer-assisted synthesis [9]. Also, Zhang et al. have applied nanofiber seeding to synthesize PANI nanofibers [10]. Despite all of these synthetic efforts, there is a need for a benign and practical synthetic route capable of making pure, uniform motif in bulk quantities.

SC CO_2 has been extensively studied for chemical reactions, material synthesis and separations because it is environmental benign and minimizes the liquid waste problem [11]. SC CO_2 can dissolve solutes and yet possesses low viscosity, high diffusivity and zero surface tension. Moreover, SC CO_2 solvation power can be tuned by changing temperature and pressure. Meanwhile, unreacted materials and byproducts can be easily removed from the system; thus high purity is possible.

In the present paper, we report a new route to prepare PANI microtubes via polymerization at the interface of SC CO_2/aqueous solution. The synthesis is based on the well-known chemical oxidative polymerization of aniline in an acidic environment with APS as the oxidant [12], and surfactant SDS was used as the template. The main characteristic of this route is that the monomer aniline which is dissolved in SC CO_2 phase, slowly polymerized at the interface of SC CO_2/aqueous solution to form the PANI microtubes.

2. Experimental section

2.1. Materials

Aniline, sodium dodecyl sulfate (SDS), ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) (ASP) provided by Beijing Chemical Reagent Company were all analytical grade. Carbon dioxide (99.95%) was supplied by Beijing Analytical Factory.

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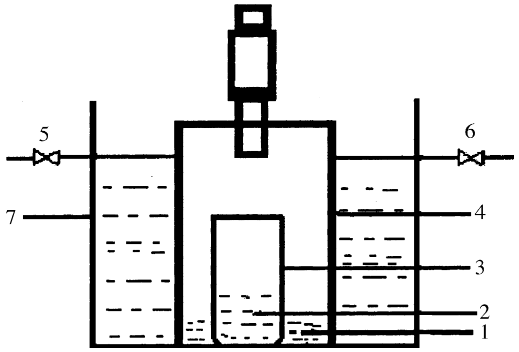


Fig. 1. Schematic diagrams of the apparatus: (1) aniline, (2) aqueous solution, (3) beaker, (4) view autoclave, (5, 6) valve, (7) water bath.

2.2. Synthesis of PANI microtubes

In a typical experiment, 0.9 ml aniline was injected into the view autoclave with an internal volume of 58 ml. The solution with 8 ml deionized water, 10.0 mmol APS, 5.0 mmol SDS and 10 μl hydrochloric acid (1 M) was prepared in a 20 ml beaker. The beaker was placed into the view autoclave. The aniline did not contact with the aqueous solution, as shown in Fig. 1. The view autoclave was then placed in the constant temperature water bath of 323.2 K, and CO_2 was compressed into the view autoclave up to the 8.5 MPa using a high-pressure syringe pump (Model DB-80). Aniline was dissolved in SC CO_2 and slowly polymerized at the SC CO_2/aqueous solution interface. After 12 h, the entire aqueous phase is filled with dark-green PANI. After releasing CO_2, the aqueous was centrifuged. The obtained product was washed several times with deionized water and ethanol. Finally the product was dried in a vacuum oven at 323 K for 12 h.

2.3. Characterization

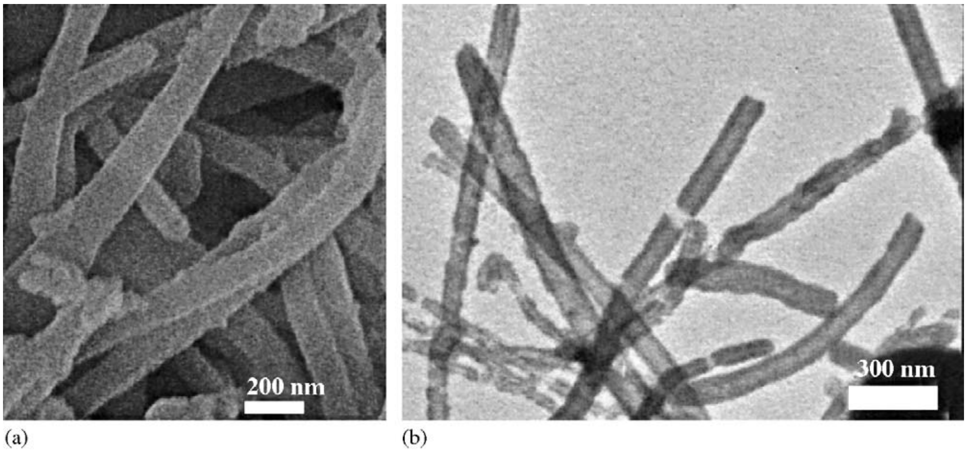
The morphology of the PANI structures was characterized by scanning electron microscopy (SEM, Hitachi-530) and transmission electron microscopy (TEM, Hitachi, H-9000). A TU-1201 spectrophotometer was used to determine the UV–vis spectra of PANI in deionized water. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX2500, Rigaka) with Cu Kα radiation (λ = 1.5406 Å). The IR spectrum was recorded using an IR spectrometer (TENSOR 27). X-ray photoelectron spectra (XPS) was performed on ES-300 (Kratos). The conductivity at room temperature was measured by a Keithley 196 SYSTEM DM digital multimeter and an ADVANTEST R6142 programmable dc voltage/current source through a standard four-probe method.

3. Results and discussion

The SEM and TEM micrographs of the PANI samples synthesized at 323.2 K and 8.5 MPa are shown in Figs. 2a and 2b. It is demonstrated that the PANI products obtained have diameters with about 120 nm and lengths of around several micrometers (Fig. 2a). Interestingly, it is clearly seen from the TEM image (Fig. 2b) that PANI products display hollow core due to the distinct color difference between the shell and inner region.

In order to make sure the PANI degree of the crystllinity, Fig. 3 shows that two broad peaks centered at $2\theta = 20°$ and 24.8° appear in the XRD pattern of the composite, which shows the resulting PANI microtubes are amorphous [13]. The peak at $2\theta = 20°$ may be ascribed to periodicity parallel to the polymer chain, while the peak at $2\theta = 24.8°$ may be caused by the periodicity perpendicular to the polymer chain [14].

It is well known that PANI has a simple and reversible acid/base (doping/dedoping) chemistry enabling control of its properties, such as electrical conductivity [3] and optical activity [15]. By observation, the doped and dedoped PANI complexes form green and blue suspensions in aqueous solution, respectively. The UV–vis spectra of the doped and dedoped PANI microtubes are shown in Fig. 4. The characteristic bands of doped PANI appear at 326, 418, and 850 nm with a free carrier tail extending into the near-infrared region, which were attributed to π-π^*, polaron-π^*, and π-polaron transitions, respectively [16]. For the dedoped form, there exist two peaks at around 320 and 674 nm in the UV–vis spectra. However, the band of the dedoped PANI microtubes of this work at 674 nm is wider than those reported by other authors [3,17], which may result from the difference in morphology and size.



(a) (b)

Fig. 2. SEM (a) and TEM (b) images of synthesized PANI microtubes.